

ANSWER 1 OF 4 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1998:8627 CAPLUS

DN 128:61255

ED Entered STN: 08 Jan 1998

TI Decomposition inhibitors containing 1-oxypiperidines and inhibition of decomposition of chlorohydrocarbons by using them

IN Nakashima, Sadao; Tanisaki, Seiji; Nakamura, Shutaro

PA Hakuto K. K., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM C07C019-01

ICS C07C017-42; C07C021-18

CC 23-3 (Aliphatic Compounds)

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 09328444	A2	19971222	JP 1996-145880	19960607 <--
PRAI	JP 1996-145880		19960607		
OS	MARPAT 128:61255				
AB	The title inhibitors are useful in preparation, purification, and storage of chlorohydrocarbons. 1,1,1-Trichloroethane was refluxed with FeCl <sub>3</sub> and 100 ppm 2,2,6,6-tetramethylpiperidine-1-oxyl for 1 h to form 0.2% vinylidene chloride (99% decomposition inhibition).				
ST	oxypiperidine inhibitor decompn chlorohydrocarbon; chloroethane decompn inhibitor methylpiperidinyloxyl				
IT	Decomposition Stabilizing agents (1-oxypiperidines for decomposition inhibition of chlorohydrocarbons)				
IT	Hydrocarbons, miscellaneous RL: MSC (Miscellaneous) (chloro; 1-oxypiperidines for decomposition inhibition of chlorohydrocarbons)				
IT	2226-96-2, HTEMPO	2516-92-9	2564-83-2, TEMPO	6599-87-7	200433-13-2
	RL: MOA (Modifier or additive use); USES (Uses) (1-oxypiperidines for decomposition inhibition of chlorohydrocarbons)				
IT	71-55-6, 1,1,1-Trichlorethane RL: MSC (Miscellaneous) (1-oxypiperidines for decomposition inhibition of chlorohydrocarbons)				

L33 ANSWER 2 OF 4 INPADOC COPYRIGHT 2004 EPO on STN

LEVEL 1

AN 103691621 INPADOC EW 199807 UW 199818

TI DEGRADATION RETARDER OF CHLORINATED HYDROCARBON AND RETARDATION OF DEGRADATION.

IN NAKAJIMA SADA0; TANIZAKI SEIJI; NAKAMURA SOTARO

INS NAKAJIMA SADA0; TANIZAKI SEIJI; NAKAMURA SOTARO

PA HAKUTO CO LTD

PAS HAKUTO KK

TL English

DT Patent

PIT JPA2 DOCUMENT LAID OPEN TO PUBLIC INSPECTION

PI **JP 09328444** **A2 19971222**

AI JP 1996-145880 A 19960607

PRAI JP 1996-145880 A 19960607

OSCA 128:061255

OSDW 98-105091

ICM (6) C07C019-01

ICS (6) C07C017-42; (6) C07C021-18

L33 ANSWER 3 OF 4 JAPIO (C) 2004 JPO on STN

AN 1997-328444 JAPIO  
 TI DEGRADATION RETARDER OF CHLORINATED HYDROCARBON AND RETARDATION OF  
 DEGRADATION  
 IN NAKAJIMA SADA0; TANIZAKI SEIJI; NAKAMURA SOTARO  
 PA HAKUTO CO LTD  
 PI JP 09328444 A 19971222 Heisei  
 AI JP 1996-145880 (JP08145880 Heisei) 19960607  
 PRAI JP 1996-145880 19960607  
 SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1997  
 IC ICM C07C019-01  
 ICS C07C017-42; C07C021-18  
 AB PROBLEM TO BE SOLVED: To obtain degradation retarder of a chlorinate  
 hydrocarbon comprising piperidine-1-oxyl group, capable of efficiently  
 retarding a degradation of chlorinated hydrocarbons when purifying by a  
 distillation or storing.  
 SOLUTION: This degradation retarder consists essentially of  
 piperidine-1-oxyl group of formula I, II, III and IV (R<SP>1</SP> is a  
 1-3C alkyl; R<SP>2</SP> is H, OH or OR<SP>3</SP>; R<SP>3</SP> is a 1-3C  
 alkyl or phenyl; R<SP>4</SP> is H or a 1-17C alkyl; X is a 1-8C alkylene  
 or phenylene). The addition amount of the compound based on the amount of  
 the chlorinated hydrocarbon is 0.05-200wt.ppm, especially 1-20wt.ppm. The  
 piperidine-1-oxyl group prevents the plugging of the pipeline of a  
 distillation equipment because not forming a solid salt and can  
 efficiently retard the degradation of the chlorinated hydrocarbon so can  
 improve the purity of the chlorinated hydrocarbons further stabilize the  
 process and facilitate a safety operation of the equipment.  
 COPYRIGHT: (C)1997,JPO

L33 ANSWER 4 OF 4 WPIDS COPYRIGHT 2004 THOMSON DERWENT on STN

AN 1998-105091 [10] WPIDS

DNC C1998-034822

TI Decomposition inhibitors for chloro-hydrocarbon(s) - comprise  
 piperidine-1-oxyl as main component, added during production/purification  
 or storage to increase purity, facilitate stabilisation of process and  
 ensure safety operation of apparatus.

DC E13 E19

PA (HAKU-N) HAKUTO KK

CYC 1

PI JP 09328444 A 19971222 (199810)\* 4p C07C019-01 <--

ADT JP 09328444 A JP 1996-145880 19960607

PRAI JP 1996-145880 19960607

IC ICM C07C019-01

ICS C07C017-42; C07C021-18

AB JP 09328444 A UPAB: 19980309

Decomposition inhibitors (II) for chlorohydrocarbons (I) comprise  
 piperidine-1-oxyl as the main component. Also claimed is a method for  
 inhibition of decomposition of (I) comprising adding (II) during the  
 production/purification or storage of (I).

MORE SPECIFICALLY - (I) are 1-10C optionally saturated and  
 optionally cyclic ones and (II) are selected from (IIa)-(IId). R1 = 1-3C  
 alkyl; R2 = H, OH or OR3; R3= 1-3C alkyl or phenyl; R4 = H, 1-17C alkyl;  
 and X = 1-8C alkylene or phenylene.

ADVANTAGE - Decomposition of (I) during their  
 distillation/purification or storage can be efficiently suppressed to  
 increase their purity and facilitate stabilisation of the process and  
 ensure safety operation of the apparatus.

Dwg.0/0

FS CPI

FA AB; GI; DCN

MC CPI: E07-D05; E10-H03C

=>

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-328444

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(51)Int.Cl.

C07C 19/01

C07C 17/42

C07C 21/18

(21)Application number : 08-145880

(71)Applicant : HAKUTO CO LTD

(22)Date of filing : 07.06.1996

(72)Inventor : NAKAJIMA SADAO

TANIZAKI SEIJI

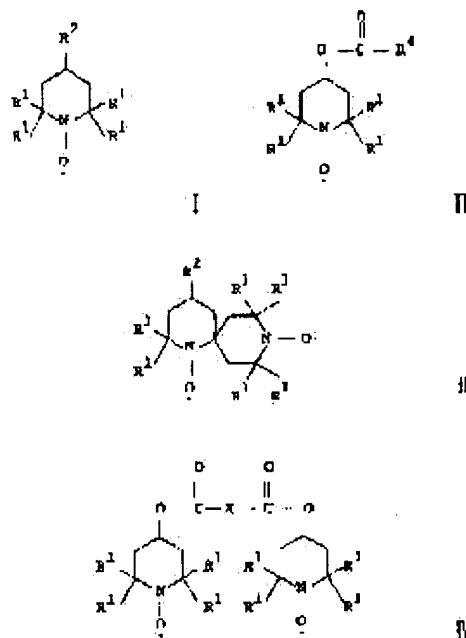
NAKAMURA SOTARO

## (54) DEGRADATION RETARDER OF CHLORINATED HYDROCARBON AND RETARDATION OF DEGRADATION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain degradation retarder of a chlorinate hydrocarbon comprising piperidine-1-oxyl group, capable of efficiently retarding a degradation of chlorinated hydrocarbons when purifying by a distillation or storing.

SOLUTION: This degradation retarder consists essentially of piperidine-1-oxyl group of formula I, II, III and IV (R<sup>1</sup> is a 1-3C alkyl; R<sup>2</sup> is H, OH or OR<sup>3</sup>; R<sup>3</sup> is a 1-3C alkyl or phenyl; R<sup>4</sup> is H or a 1-17C alkyl; X is a 1-8C alkylene or phenylene). The addition amount of the compound based on the amount of the chlorinated hydrocarbon is 0.05-200wt.ppm, especially 1-20wt.ppm. The piperidine-1-oxyl group prevents the plugging of the pipeline of a distillation equipment because not forming a solid salt and can efficiently retard the degradation of the chlorinated hydrocarbon so can improve the purity of the chlorinated hydrocarbons further stabilize the process and facilitate a safety operation of the equipment.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

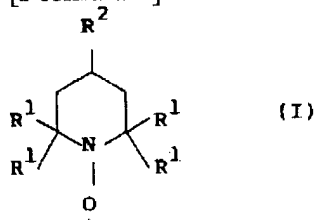
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[Claim(s)]

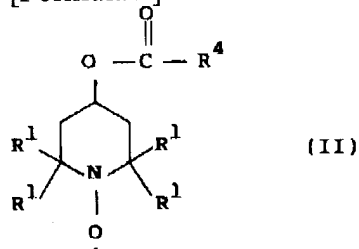
[Claim 1] The decomposition inhibitor of the chlorinated hydrocarbon which uses piperidine-1-oxyl as a principal component.

[Claim 2] Piperidine-1-oxyl The following general formula (I), (II), (III), (IV) The alkyl group of carbon numbers 1-3 and R<sub>2</sub> among [type R<sub>1</sub> H, an OH radical, or three OR (R<sub>3</sub> is the alkyl group or phenyl group of carbon numbers 1-3), It is the decomposition inhibitor of the chlorinated hydrocarbon according to claim 1 which is at least one sort of the compound group shown by] R<sub>4</sub> indicates the alkyl group of H or carbon numbers 1-17, and X indicates the alkylene group or phenylene group of carbon numbers 1-8 to be.

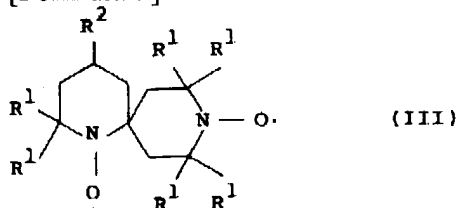
[Formula 1]



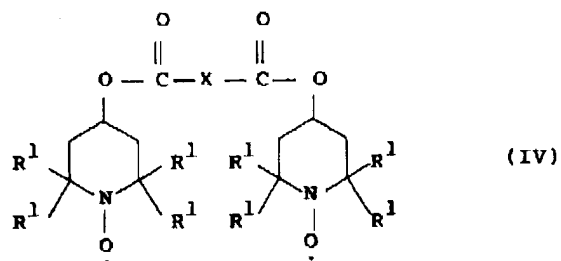
[Formula 2]



[Formula 3]



[Formula 4]



[Claim 3] The decomposition control approach of the chlorinated hydrocarbon characterized by adding piperidine-1-oxyl according to claim 1 or 2 in this chlorinated hydrocarbon in manufacture, purification, and the storage facility of chlorinated hydrocarbon.

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the decomposition control approach in the decomposition inhibitor of chlorinated hydrocarbon and manufacture of chlorinated hydrocarbon, purification, and a storage process.

[0002]

[Description of the Prior Art] Chlorinated hydrocarbon is widely used in the industrial world as a solvent or a washing solvent as a raw material of various petrochemicals. These chlorinated hydrocarbon does not have the enough stability over heat or light, and it is especially known for the quality of an impurity of moisture and an acid component, and existence of Lewis acid still like the ferric chloride of a minute amount that decomposition will be promoted remarkably. Decomposition of chlorinated hydrocarbon brings about many evils, such as decline in about [ worsening product purity with the decomposition product ] and product generation yield, and breakage on the device by the hydrogen chloride further produced with decomposition. In order to control this decomposition, the approach of adding alkaline substances, such as a sodium carbonate and amines (for example, JP,6-92324,B), is learned.

[0003]

[Problem(s) to be Solved by the Invention] However, also when alkaline substances, such as a sodium carbonate and amines, reacted with the hydrogen chloride to generate, a solid salt was generated, and this brought about closeout of piping of a distillation apparatus or was used as a solvent or a washing solvent, the actual condition had connoted evils, such as bringing about contamination.

[0004] The object of this invention controls distillation purification of these chlorinated hydrocarbon, and the decomposition in the case of storage, raises the purity of chlorinated hydrocarbon, and is to offer the decomposition inhibitor and the decomposition control approach for making stabilization of a process, and a safety operation of equipment easy.

[0005]

[Means for Solving the Problem] As a result of considering the decomposition device of these chlorinated hydrocarbon and repeating examination wholeheartedly about development of a decomposition inhibitor new type, this invention persons find out that piperidine-1-oxyl agrees for this object, and a solid salt moreover is not generated, therefore closeout of piping of a distillation apparatus is not brought about, and decomposition can be controlled very efficiently, and came to make this invention.

[0006] That is, this inventions are the decomposition inhibitor of the chlorinated hydrocarbon which uses piperidine-1-oxyl as a principal component, and the decomposition control approach of chlorinated hydrocarbon using this.

[0007]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

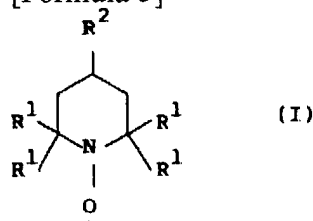
[0008] The chlorinated hydrocarbon in this invention is the shape of a chain and the annular chlorinated

hydrocarbon of carbon numbers 1-10. Specifically Methyl chloride, a methylene chloride, chloroform, Chlorinated-hydrocarbons [ of the carbon number 1 of a carbon tetrachloride ], ethyl chloride, 1, and 1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1 and 1, 2-trichloroethane, 1, 1, 1, 2 tetrachloroethane, 1, 1 and 2, 2-tetrachloroethane, The chlorination saturated hydrocarbon of the carbon number 2 of pentachloroethane and hexa chloroethane, A vinyl chloride, a vinylidene chloride, transformer dichloro ethylene, SHISU dichloro ethylene, The chlorination unsaturated hydrocarbon of the carbon number 2 of trichloroethylene and perchloroethylene, It is annular chlorinated hydrocarbon, such as the chlorination saturated hydrocarbon of a carbon number 3, such as a mono-KURORU propane, a dichloro propane, a TORIKURORU propane, and a KURORU propylene, chlorination unsaturated hydrocarbon and clo RUPENZEN, dichloro PENZEN, chlorotoluene, and KURORU naphthalene.

[0009] The piperidine-1-oxyl in this invention is the compounds preferably shown by the general formula (I), (II), (III), and (IV).

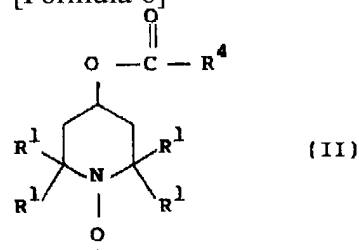
[0010]

[Formula 5]



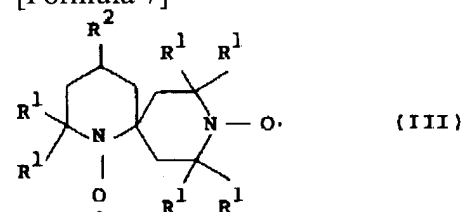
[0011]

[Formula 6]



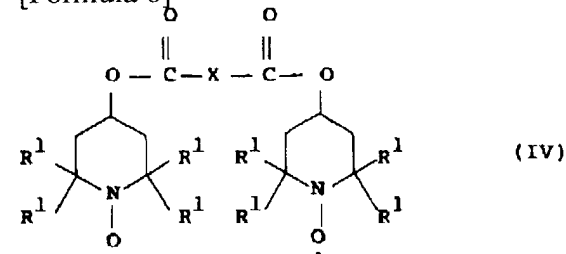
[0012]

[Formula 7]



[0013]

[Formula 8]





[0014] R1 is a methyl group, an ethyl group, n-propyl group, and an iso-propyl group at the alkyl group of carbon numbers 1-3, and a concrete target. R2 is H, an OH radical, or three OR, R3 is the alkyl group or phenyl group of carbon numbers 1-3, and the alkyl groups of carbon numbers 1-3 are specifically a methyl group, an ethyl group, n-propyl group, and an iso-propyl group. R4 is the alkyl group of H or carbon numbers 1-17, and the alkyl groups of carbon numbers 1-17 are specifically a methyl group, an ethyl group, n-propyl group, butyl, a pentyl (amyl) radical, a hexyl group, an octyl radical, a nonyl radical, a decyl group, the dodecyl, a heptadecyl radical, etc. X is the alkylene group or phenylene group of carbon numbers 1-8, and, specifically, the alkylene groups of carbon numbers 1-8 are a methylene group, ethylene, a propylene radical, a hexylene radical, etc.

[0015] When such piperidine-1-oxyl is illustrated concretely, 2, 2, 6, and 6-tetramethylpiperidine-1-oxyl, 2, 2, 6, and 6-tetramethyl-4-hydroxy piperidine-1-oxyl, 2, 2, 6, and 6-tetramethyl-4-methoxy piperidine-1-oxyl, 2, 2, 6, and 6-tetramethyl-4-ethoxy piperidine-1-oxyl, 2, 2, 6, and 6-tetramethyl-4-phenoxy piperidine-1-oxyl, 2, 2, 6, and 6-tetramethyl-4-carboxy piperidine-1-oxyl, 2, 2, 6, and 6-tetramethyl-4-acetoxy piperidine-1-oxyl, 1, 9-diaza - 2, 2, 8, 8, 10, 10-hexa METERU-4-HIDOROKIN-spiro [5.5] undecane -1, 9-JIOKISHIRU, screw (2, 2, 6, and 6-tetramethyl-4-piperidyl)-N, and N'-JIOKI sill sebacate is mentioned.

[0016] The thing same often [ application of the piperidine-1-oxyl in this invention / dissolving one sort of these piperidines-1-oxyl or two sorts or more in a suitable solvent, and adding ] and preferably as target chlorinated hydrocarbon is used for a solvent.

[0017] although the addition of piperidine-1-oxyl cannot change with operating conditions of the class of target chlorinated hydrocarbon, the target manufacture, purification, and a storage facility etc. and cannot generally be limited -- general -- chlorinated hydrocarbon -- receiving -- the 0.05 - 200 weight ppm -- desirable -- the 0.5 - 20 weight ppm -- it is the 1 - 20 weight ppm still more preferably. Although there is effectiveness of enough when [ than the another side 200 weight ppm ] more [ the object of this invention will not fully be demonstrated if fewer than the 0.05 weight ppm, and ], effectiveness does not become large considering an addition and it is not desirable from an economical standpoint.

[0018] Piperidine-1-oxyl is added in the upper section of the problem part or a problem part so that it may exist in the part where chlorinated hydrocarbon decomposes and becomes an issue. For example, generally, since it is easy to decompose in a distilling column, it is suitable for chlorinated hydrocarbon to add the feeding line of a distilling column and near the overhead section best stage of a distilling column.

[0019] Moreover, in order to control the decomposition under storage of chlorinated hydrocarbon, PIPERISHIN-1-oxyl is added before storing chlorinated hydrocarbon.

[0020] In case disassembly of chlorinated hydrocarbon is controlled using the piperidine-1-oxyl of this invention, in the range which does not spoil the effectiveness of this invention, concomitant use with other known decomposition inhibitors and radical polymerization inhibitor is not barred.

[0021] Since the mechanism of action of decomposition control to the chlorinated hydrocarbons of the piperidine-1-oxyl of this invention is considered that disassembly of chlorinated hydrocarbons advances by the radical chain reaction, it is presumed that the free radical part which is dwelling in the intramolecular of the piperidine-1-oxyl compound of this invention stops the radical chain of decomposition suitably. Although the compound which generally acts on a radical and is made to stop a radical chain has some which are known as radical polymerization inhibitor, the typical compound is not done so in some decomposition control effect end so that clearly from the example of a comparison collectively shown in the after-mentioned example, but a surprising thing has [ the effectiveness of the piperidine-1-oxyl of this invention is remarkable, and ] it. [ high ]

[0022]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to this. In addition, the brief sketch used in the example and the example of a comparison shows the following compound, respectively.

[0023] [The compound used for the example]

TEMPO: The 10-hexa methyl-[ 2, 2 and 6, 6-tetramethylpiperidine-1-oxyl HTEMPO:2, 2 and 6 6-

tetramethyl-4-HITOROKISHI piperidine-1-oxyl AcTEMP:2, 2 and 6, 6-tetramethyl-4-acetoxy piperidine-1-oxyl DAHMHUSUDO:1, 9-diaza -2, 2, 8, 8 and 10, and ]4-hydroxy SUPIRO [5 [ 5 and ]]-undecane -1, 9-JIOKISHIRU BTEMPOSAT: Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl)-N and N-JIOKI sill sebacate [0024] [The compound used for the example of a comparison]

NSP:p-nitrosophenol TBC:p-tertiary butyl catechol HTEMP:2, 2 and 6, and 6-tetramethyl-4-hydroxy piperidine [0025] 1,1,1-trichloroethane 300mL was put into the 500mL flask with [test-condition] reflux equipment, and specified quantity addition of 0.5g of ferric chlorides and the piperidine-1-oxyl was carried out here. Content liquid was extracted after 1-hour heating reflux, and the yield of a vinylidene chloride was searched for by gas chromatography KURAFU. Since 1,1,1-trichloroethane became a vinylidene chloride and a hydrogen chloride when it decomposed, it had the yield of a vinylidene chloride and made it the cracking severity of 1,1,1-trichloroethane.

[0026]

[Equation 1]

$$\text{分解抑制率 (\%)} = \frac{\left( \begin{array}{c} \text{薬品無添加時の} \\ \text{塩化ビニリデン生成率} \end{array} \right) - \left( \begin{array}{c} \text{薬品添加時の} \\ \text{塩化ビニリデン生成率} \end{array} \right)}{\left( \begin{array}{c} \text{薬品無添加時の塩化ビニリデン生成率} \end{array} \right)} \times 100$$

[0027] A result is as having been shown in a table 1, and it turns out that decomposition of 1,1,1-trichloroethane was effectively controlled by addition of the piperidine-1-oxyl of this invention.

[0028]

[A table 1]

		化 合 物	添加量* (ppm)	塩化ビニリデン 生成率 (%)	分解抑制率 (%)
実 施 例	1	TEMPO	5	5.9	67
	2	TEMPO	10	2.9	84
	3	TEMPO	100	0.2	99
	4	HTEMP	5	7.5	58
	5	HTEMP	10	4.5	75
	6	AcTEMP	10	5.0	72
	7	DAHMHUSUDO	10	5.7	68
	8	BTEMPOSAT	10	7.9	56
	9	TEMPO HTEMP	5 5	3.6	80
比 較 例	1	無添加 (ブランク)	—	18.0	(基準)
	2	NSP	100	16.7	7
	3	TBC	100	17.6	2
	4	HTEMP	100	15.1	16

注：\*…添加量は1,1,1-トリクロロエタンに対する重量ppmである。

[0029]

[Effect of the Invention] As explained above, according to this invention, distillation purification of chlorinated hydrocarbon and the decomposition in the case of storage can be controlled efficiently, the purity of chlorinated hydrocarbon can be raised, and stabilization of a process and a safety operation of equipment can be made easy.

[Translation done.]